

ULTRASENSITIVE DETECTION OF ATMOSPHERIC TRACE GASES  
USING FREQUENCY MODULATION SPECTROSCOPY

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Frequency modulation (FM) spectroscopy is a new technique that promises to significantly extend the state-of-the-art in point detection of atmospheric trace gases. First introduced in the visible spectral region by Bjorklund (1980), FM spectroscopy is essentially a balanced bridge optical heterodyne approach in which a small optical absorption or dispersion from an atomic or molecular species of interest generates an easily detected radio frequency (rf) signal. This signal can be monitored using standard rf signal processing techniques and is, in principle, limited only by the shot noise generated in the photodetector by the laser source employed. The use of very high ( $\sim$  GHz) modulation frequencies which exceed the spectral width of the probed absorption line distinguishes this technique from the well-known derivative spectroscopy which makes use of low (kHz) modulation frequencies.

FM spectroscopy has recently been extended to the 10- $\mu$ m infrared (IR) spectral region where numerous polyatomic molecules exhibit characteristic vibrational-rotational bands [Cooper and Gallagher, 1985]. In conjunction with tunable semiconductor diode lasers, the quantum-noise-limited sensitivity of the technique should allow for the detection of absorptions as small as  $10^{-8}$  in the IR spectral region. This sensitivity would allow for the detection of  $H_2O_2$  at concentrations as low as 1 pptv with an integration time of 10 seconds. In this workshop we briefly discussed the principles of the technique and the major technical obstacles that must be overcome to achieve quantum-noise-limited sensitivity.

#### REFERENCES

Bjorklund, G.C., "Frequency-Modulation Spectroscopy: A New Method for Measuring Weak Absorptions and Dispersions," Optics Letters, Vol. 5, p. 15, 1980.

Cooper, D.E., and T.F. Gallagher, "Frequency Modulation Spectroscopy with a  $CO_2$  Laser: Results and Implications for Ultrasensitive Point Monitoring of the Atmosphere," Applied Optics, Vol. 24, p. 710, 1985.

## Comments

This method can be applied to both OH, operating in the near ultraviolet with a frequency doubled dye laser, and to HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> using an infrared laser, such as the diode laser discussed below.

Frequency modulation absorption was seen as a technique which has good future potential as an atmospheric detection method. At the present time, it has been demonstrated at the  $10^{-4}$  level of detectable absorption in laboratory experiments, whereas  $10^{-7}$  will be needed in a field instrument in order to be generally useful for atmospheric monitoring. The obstacles to future development comprise a long list of technical issues, which are likely to be solved with further improvements in laser and modulation devices.

Thus, the workshop participants generally agreed that FM spectroscopy was not currently ready for full-scale instrument development, in order to make field measurements of OH in a few-year time scale. Concern was expressed as to whether it would ever be capable of measuring OH in the near future. However, its general applicability to a wide variety of atmospheric species makes it a very attractive and logical extension of absorption methods. Well-designed experiments examining the best spectral regions for study along with a systematic investigation of pressure effects (line broadening) should be considered for funding. Collaboration between researchers experienced in atmospheric absorption spectroscopy and those knowledgeable about FM methods should be encouraged. Steps should be taken toward laboratory measurements on typical air samples.